III.A.2 Oxidation Resistant, Cr Retaining, Electrically Conductive Coatings on Metallic Alloys for SOFC Interconnects

Vladimir Gorokhovsky
Arcomac Surface Engineering, LLC
151 Evergreen, Suite D
Bozeman, MT 59715
Phone: (406) 522-7620; Fax: (406) 522-7617; E-mail: vigase@aol.com

DOE Project Manager: Travis Shultz
Phone: (304) 285-1370; E-mail: Travis.Shultz@netl.doe.gov

Objectives

- Enable the use of inexpensive metallic alloys as planar solid oxide fuel cell (SOFC) interconnects via protective coatings.
- Develop and demonstrate novel, cost-effective deposition processes to establish dense and uniform protective and functional coatings on metallic substrates.
- Evaluate protective coatings during exposures relevant to SOFC interconnects.
- Optimize deposition process parameters to maximize SOFC metallic interconnect performance and ultimately reduce cost.

Approach

- Design coating deposition process formulations based upon thermodynamic modeling and prior art.
- Deposit a matrix of candidate coatings on metallic substrates of interest for SOFC interconnects.
- Evaluate coated samples during exposure to SOFC interconnect conditions.
- Analyze sample performance and optimize coating deposition processes.
- Develop coating deposition system to meet Solid State Energy Conversion Alliance (SECA) SOFC interconnect cost and performance requirements.

Accomplishments

- Reduced metallic alloy oxidation rate by an order of magnitude. Rutherford backscattering spectroscopy (RBS) results indicate stainless steel samples with un-optimized, nanolayered CrN/AlN coatings exhibit an order of magnitude increase in oxidation resistance compared to uncoated counterparts.
- Developed and tested new, hybrid coating process combining electron beam physical vapor deposition (EBPVD), thermal evaporation and filtered arc deposition (FAD) to deposit dense $(Co,Mn)_3O_4$ coatings in an economically favorable process.
- Significantly reduced Cr volatility. Un-optimized coated samples of Crofer 22 APU [1] exhibited a fifteen-fold decrease in Cr volatility compared with their uncoated counterparts. Effectively complete blocking of Cr volatility is hopeful.
- Demonstrated 2,400+ hours of low and stable area specific resistance (ASR) values. Coated stainless steel samples demonstrated low and stable ASR values in air at 800°C for over 2,400 hours in contact with Ag paste.

Future Directions

- Evaluate coated stainless steels in more prototypical SOFC interconnect operating conditions. In collaboration with SOFC developers, samples of coated stainless steel will be subjected to SOFC small stack and other relevant testing to determine in-situ performance of coated stainless steel samples.
- Analyze the SOFC interconnect related performance of coated stainless steel samples to determine best coating system(s). Subsequent to SOFC stack testing, coated stainless steel samples will undergo a myriad of surface analyses to understand protection and performance improvement mechanisms.
- Conduct combined process performance and economic evaluations to elucidate the efficacy of novel coating approaches to enable use of inexpensive metallic alloys as interconnects in planar SOFC systems.

Introduction

The Arcomac Surface Engineering, LLC (ASE) SECA project has focused on the development of protective and functional coatings to enable the use of inexpensive metallic alloys as interconnects in planar SOFC systems. Currently, the interconnect component of planar SOFC systems accounts for a dominant portion of the overall SOFC stack cost. Inexpensive metallic alloys are under consideration for this component; however, when exposed to SOFC interconnect operation, metallic alloys form blanketing oxide scales, which dramatically degrade SOFC performance and limit device lifetime. To date, deleterious issues with Cr volatility, electrical resistance, and thermal-mechanical and chemical incompatibilities have restricted the use of metallic alloys as interconnects in planar SOFC systems. ASE has developed advanced coating deposition technologies that show promise for resolving these issues in an economically viable manner.

Approach

To achieve the cost and performance goals of SECA, the use of inexpensive metallic alloys as interconnect components is under investigation. Commercially available alloys exhibit unacceptable performance during SOFC interconnect operation. ASE is developing advanced, hybrid deposition technologies to establish protective coatings on commercially available alloys of interest to the SOFC interconnect application. Desired coating compositions and architectures are determined through thermodynamic and transport modeling in addition to prior art. Appropriate deposition materials are acquired, and deposition processes are designed and executed using ASE equipment. Coated samples are tested in conditions simulating SOFC interconnect operation, and performance of the sample coupons is analyzed. Results are employed to assist in developing new coating deposition process formulations. Promising coating systems from preliminary testing are then subjected to more prototypical SOFC interconnect conditions for further technical evaluations. Concurrently, economic evaluations of the coating process and interconnect component fabrication are ongoing.

Results

Figure 1 schematically illustrates the ASE-developed Filtered Arc Plasma Source Ion Deposition (FAPSID) surface engineering system [2]. The FAPSID system is an advanced, hybrid coating deposition chamber consisting of two dual large area filtered arc sources in conjunction with two unbalanced magnetron sputtering devices, two electron beam evaporators and a thermal resistance evaporation source in one universal vacuum chamber layout. This system has demonstrated the capability to deposit nanocomposite, nanolayered coatings with a wide variety of compositions and architectures.

The present ASE two-segment hybrid coating approach is shown schematically in Figure 2. Filtered arc deposited, nanolayered coatings of CrN/AlN, as shown in the tunneling electron microscopy (TEM) image in Figure 3a, have been investigated to comprise a lower, oxidation-resistant, bond segment coating. Additional elements such as Co, Ti, Mn, Y, and O have also been investigated for use in the lower, bond segment coating. This layer is designed to function as an effective barrier, blocking both inward and outward diffusion of oxidizing species, while acting as an adhesion system to the upper coating segment. A matrix of these lower segment coatings has been successfully deposited with

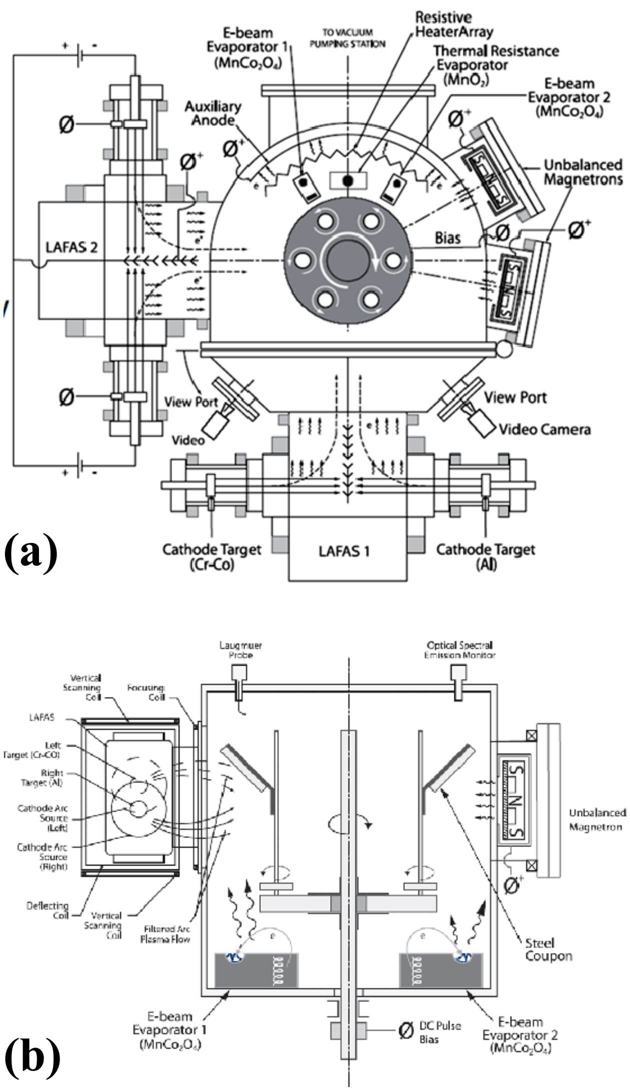

Figure 1. Schematic Illustration of the FAPSID Surface Engineering System, Showing (a) Top View and (b) Side View

excellent adhesion to metallic substrates under consideration for SOFC interconnects. Filtered arc-assisted EBPVD $(Co,Mn)_3O_4$ coatings after 800°C oxidation in air, as shown in the surface scanning electron microscopy (SEM) image in Figure 3b, comprise an electrically conductive, Cr-retentive and SOFC cathode-compatible upper coating segment. Other hybrid deposition methods employing filtered arc-assisted thermal resistance evaporation are also being explored to deposit the upper segment coating. A matrix of upper segment coatings has been successfully deposited in combination with and apart from the matrix of lower segment coating compositions.

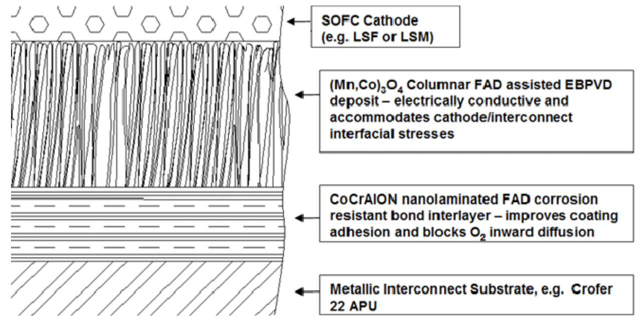

Figure 2. ASE's Two-Segment, Hybrid Coating Concept

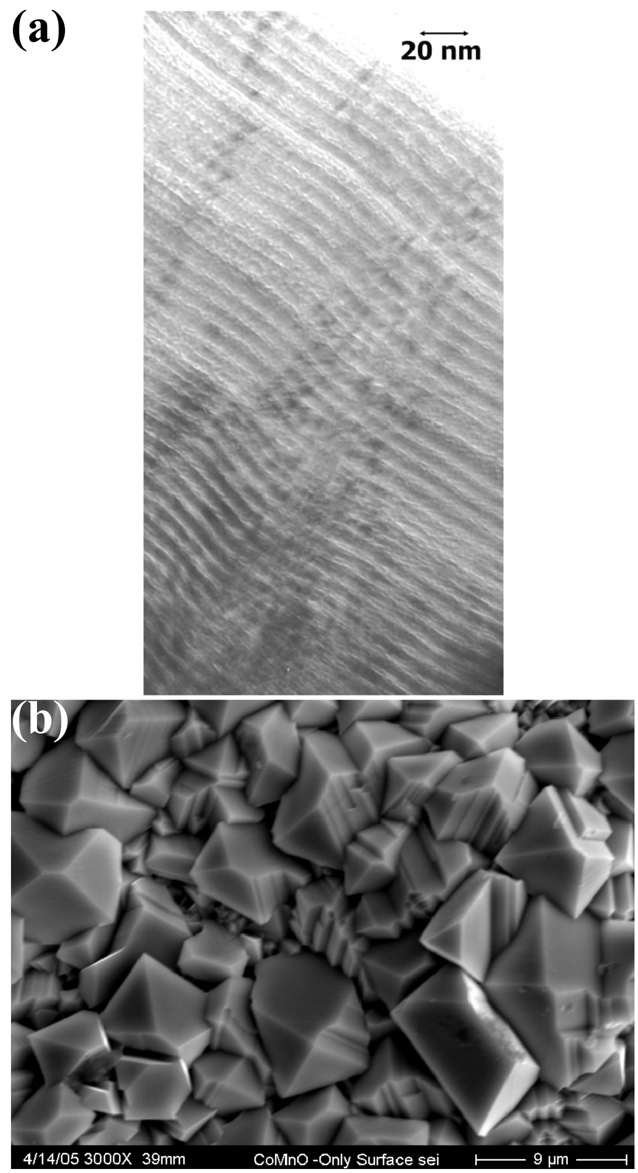

Figure 3. (a) Cross-Sectional TEM Image of FAD CrN/AlN Nanolayered Lower Segment Coating on Stainless Steel; and (b) Surface SEM Image of Filtered Arc-Assisted EBPVD $(Co,Mn)_3O_4$ Upper Segment Coating after 800°C Oxidation in Air

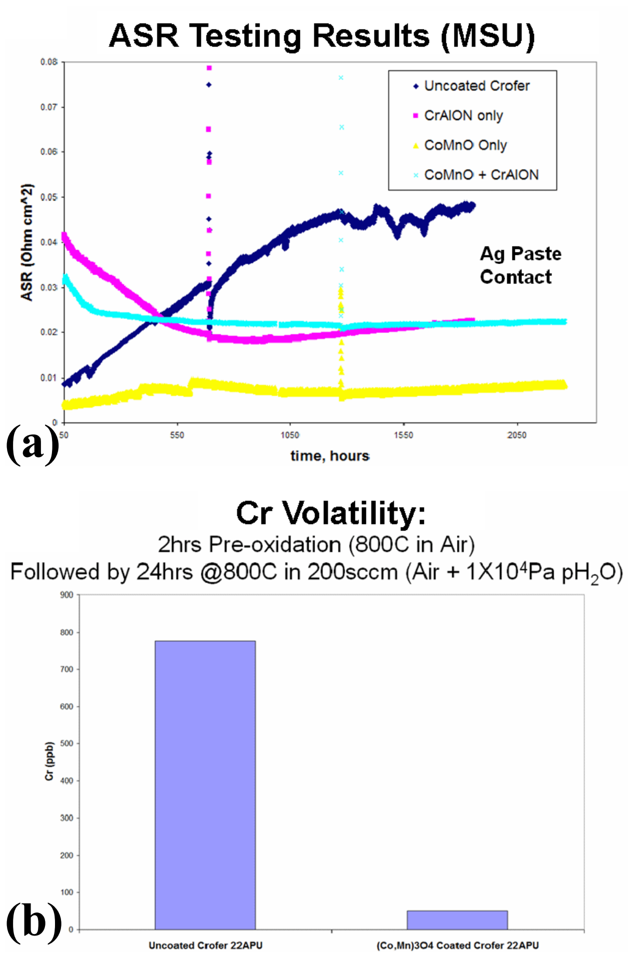

Figure 4. Summary of Preliminary ASR and Cr Volatility Results from Coated and Uncoated Crofer 22 APU

SOFC interconnect-related behavior of coated and uncoated samples—i.e., high-temperature oxidation, ASR, and Cr volatility—has been investigated in collaboration with researchers at Montana State University (MSU), Pacific Northwest National Laboratory, Lawrence Berkeley National Laboratory, and NASA-Glenn Research Center. Figure 4 displays a summary of the ASR and Cr volatility results. Low ASR values, excellent adhesion, oxidation stability and promising Cr volatility data suggest the efficacy of the ASE two-segment coating approach.

Conclusions

ASE has developed advanced coating deposition processes that may enable the use of inexpensive metallic alloys as interconnect components in planar SOFC systems. A wide variety of coating compositions and architectures is being investigated to meet SECA SOFC interconnect performance and cost requirements. A large-scale deposition system, offering favorable economics through high throughput and advanced hybrid design, is currently under development.

FY 2005 Publications/Presentations

1. "High temperature oxidation, Cr volatility and surface electrical conductivity of ferritic steel with and without filtered arc Cr-Al-O-N and/or filtered arc-assisted e-beam Co-Mn-O coatings," V.I. Gorokhovsky, Presented at the International Conference on Metallurgical Coatings and Thin Films (ICMCTF 05) in San Diego, CA, May 5, 2005
2. "Multilayer nanostructured cermet coatings for SOFC metallic interconnects," V.I. Gorokhovsky, Presented at the Sixth Annual SECA Workshop in Pacific Groove, CA, April 21, 2005
3 "Oxidation resistant, Cr retaining, conductive coatings on metallic alloys for SOFC interconnects," V.I. Gorokhovsky, Presented at the SECA Core Technology Peer Review Workshop in Tampa, FL, January 27, 2005

References

1. Crofer 22 APU "High Temperature Alloy" MSDS No. 8005 June, 2004 ThyssenKrupp VDM
2. V. Gorokhovsky, US Patent Application No.US2004/0168637 A1.